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14. ABSTRACT During the current project, we have identified classes of stable cluster motifs for implementation as building blocks of nanoenergetic materials and developed guiding principles for their synthesis. To begin, differing mechanisms that can stabilize clusters were identified. The first refers to crystal field like splitting of electronic shells via geometrical distortions that can lead to stable species at sub-shell fillings. Such a mechanism accounted for the stability of CuAl ₂₂ ⁻ and more recently, CuMg ₈ ⁻ and AuMg ₈ ⁻ . It was shown that aromaticity, traditionally used to understand stability of organic systems, can also stabilize metallic clusters. Al ₃ Bi was shown to be the first neutral all-metal aromatic species. Similar clusters containing As and Sn in place of Bi, are also stabilized by π and σ delocalized orbitals. Nanoenergetic materials need to be air stable and hence studies on the reactivity of aluminum cluster anions with water were undertaken. Theoretical investigations showed that the reactivity proceeded through Lewis acid/Lewis base pair of complementary active sites that break OH bond and clusters with two pairs of such sites generated hydrogen. These findings also led to new class of nanocatalysts that can break polar covalent bonds and recent studies showed that such pairs can even break CO bonds. Finally, protocols that can enable synthesis of clusters assembled materials were formulated by focusing on cluster assemblies made from As ₁₁ and K that contain linear and helical chains.						
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I. Introduction:

During the funding cycle, we made substantial progress in identifying new stable cluster building blocks including those stabilized by crystal field like splitting of electronic shells and through metallic aromaticity, have demonstrated that geometrically driven pairs of complementary active sites can break polar/covalent bonds, and have made headways towards synthesis of cluster nanoassemblies and their characterization. We demonstrated that the conventional shell sequence $1S^2 1P^6 1D^{10} 2S^2 1F^{14} 2P^6$ --- in spherical metal clusters leading to filled shells at electron counts 2, 8, 18, 20, 34, 40, 58, 68, 70 ...can be modified by the geometrical distortions that lead to stable species at sub-shell closings. These deformations can be looked upon as a crystal field like splitting of degenerate shells and we demonstrated this intriguing finding for the case of $CuAl_{22}^-$ cluster that exhibited enhanced stability against reaction with oxygen in experiments conducted by Castleman and co-workers at PSU. We recently extended these ideas to other stable species including $CuMg_8^-$ and $AuMg_8^-$ that exhibit stability despite the unfilled D-supershell. Their stability can be understood as a crystal field like splitting of the otherwise degenerate D shell due to internal electric fields of the positive ion cores that leads to a filled $1S^2 1P^6 1S^2 1D^8$ sequence separated by unfilled D^2 states by a large gap. We also demonstrated aromaticity as alternate mechanisms that can lead to stable cluster motifs for nanoenergetic materials. We demonstrated these intriguing findings through studies on Al_nX ($n=1-6$; $X=Bi, As, \text{ and } Sb$) clusters where Al_3Bi , Al_3As , and Al_3Sb clusters were identified as magic species. Analysis of the electronic structure revealed that these clusters had planar ground states and that their stability is rooted in the aromatic stabilization of the p-orbitals that lead to σ and π orbitals.

Designing air stable nanoenergetic materials requires a microscopic understanding of the reactivity with water. In a synergistic effort with Castleman group at PSU, we undertook a study of reactivity of aluminum cluster anions with water. It was found that unlike reactivity with oxygen that is governed by filling of electronic shells, the reactivity with water was governed by a different set of principles. These clusters were marked by Lewis-acid and Lewis-base sites and situations where these complementary sites occurred in neighboring locations, the cluster exhibited enhanced reactivity with water in a process that entailed breaking of the OH bond. Our results went farther than this as clusters that had two such pairs in neighboring locations led to the spontaneous generation of hydrogen from water. More recent work has shown that such pairs can even break OH bond in methanol and CO bond in formaldehyde. These findings not only enable control of reactivity with water to design air-stable materials, but also offer novel nano-catalysts that can yield radical pairs that can lead to fine chemicals.

Finally, we directed our efforts towards formulating the guiding principles that can lead to the generation of cluster assembled materials. In a collaborative effort with Prof. A. Sen at PSU, we generated cluster assembled materials composed of As_7 building blocks with K. We showed that by controlling the experimental conditions, one can stabilize materials that have the linear or the helical chains of arsenic and K atoms. Extensions of these to other systems is currently under study.

Since 2009, 12 group publications (GP) have resulted with support from the current AFOSR. We were invited to submit a review on our discovery of superatoms in an invited feature article in J. Phys. Chem. Our work on reactivity with water appeared in SCIENCE and drew wide recognition from news media all around the world. In the following, we give a brief summary of our accomplishments and main findings.

II. Brief Overview of Current Activities and Recent Accomplishments:

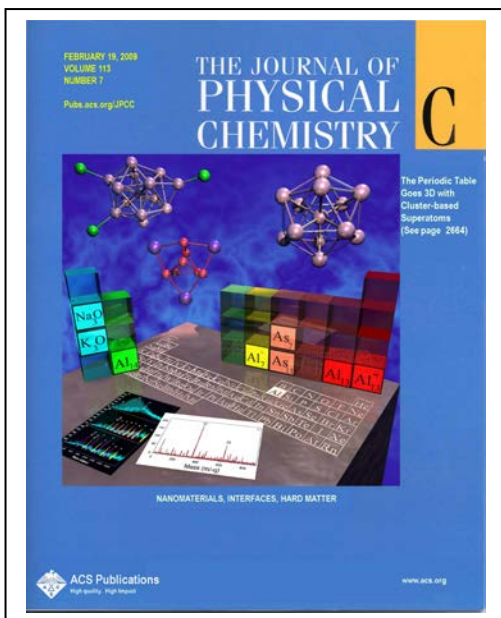


Fig. 1. Periodic table of cluster element superatoms.

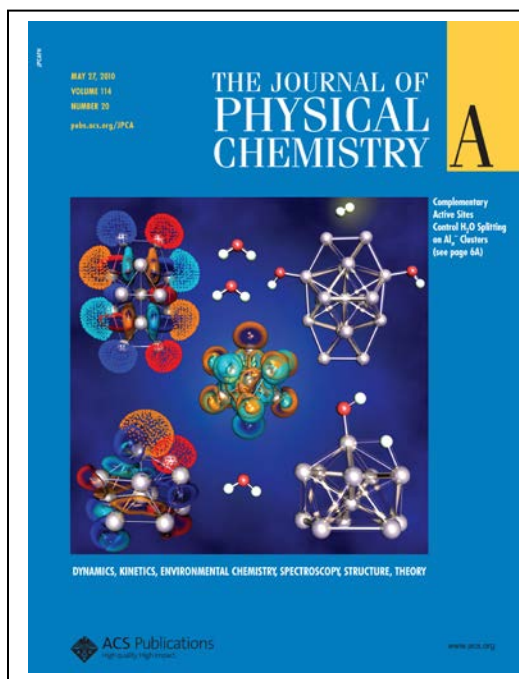


Fig. 2. Complementary active sites for reactivity of H₂O with Al_n⁺ clusters.

II. A. Summary:

While the present grant started in May 2009, we are listing the accomplishments from Jan. 2009-Dec. 2011 to make it a full year.

- ◇ *12 papers (published and submitted) in refereed journals (including 1 in SCIENCE and an invited feature article on Superatoms in J. Phys. Chem. C).*
- ◇ *Co-Chaired the Organization an International Conference on “Theory of Atomic and Molecular Clusters” in Mexico City and another in Allahabad India*
- ◇ *Gave 25 invited talks at National/International Conferences and Universities.*
- ◇ *Gave two Plenary Talks at International conferences in Mexico and India.*
- ◇ *Work featured in multiple News Media around the world*
- ◇ *A Ph. D. students supported partially graduated.*
- ◇ *Recipient of the 2010 Distinguished Scholarship Award of the Virginia Commonwealth University.*
- ◇ *Elected Fellow of the American Association for Advancement of Science.*

II. B. Highlights of Research Accomplishments:

A. Crystal Field Like Splitting of Electronic Supershells in Aluminum-Copper Anions.

As mentioned before, electronic shells in compact spherical clusters are grouped into $1S^2 1P^6 1D^{10} 2S^2 1F^{14} 2P^6$ --- sequence (see Fig. 3) and clusters with filled shells at electron counts 2, 8, 18, 20, 34, 40, 58, 68, 70 ... show features including stability, low reactivity and high ionization potential. The analogy between shells in clusters and atoms led to the concept of superatoms that now include Al_{13} , BAl_{12} , Al_{14} , Al_7^- , As_7^{3-} mimicking behaviors of halogen, alkaline earth, multivalent species. More recently, we have proposed an extension to Magnetic Superaatoms providing fundamental insight into creating Hund's like coupling in supershells to stabilize magnetic species.

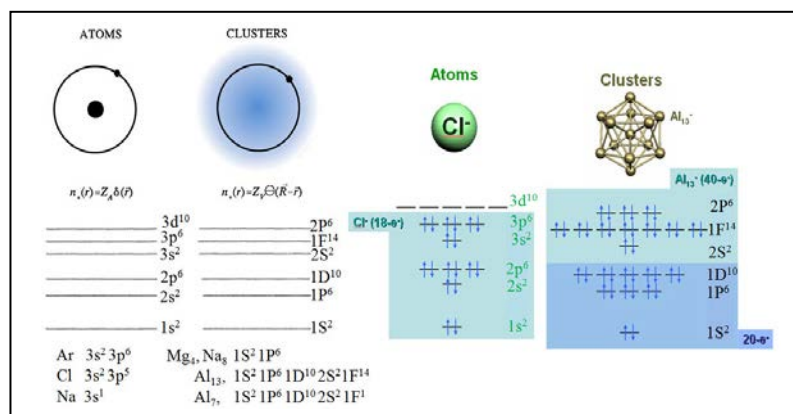


Fig. 3. Electronic shells in atoms and clusters.

Our recent joint work^{GP8} on CuAl_n^- (with Castleman and co-workers) brought out another approach to stability at sub-shell fillings. We showed that the electronic shells in clusters can undergo splitting by the potential of the ionic cores that is analogous to crystal field splitting in atoms. Measurements of the relative reactivity of CuAl_n^- clusters ($n=11-34$) with O_2 showed an alteration of the reactivity between clusters containing even/odd number of electrons with enhanced reactivity of odd electron clusters, and with CuAl_{22}^- as an unusually stable cluster (see Fig. 4). We had earlier shown that the reduced reactivity of clusters with even number of electrons is due to the conservation of electronic spin angular momentum and the triplet ground state of O_2 . Spin conservation requires that the aluminum cluster accommodate the excess spin of O_2 for an etching reaction to occur. We had proposed that a quasi-statically approximated quantity, which we refer to as the Vertical Spin Excitation Energy (VSE), is appropriate for predicting or explaining the reactivity of an aluminum containing cluster with oxygen. The VSE of a cluster with a singlet ground state is calculated as the energy difference of the ground state geometry with singlet and triplet spin multiplicities. The VSE is related to the HOMO-LUMO gap in singlet clusters. Doublet species, with an unpaired electron, all etch quickly because the spins can pair in either direction. While this could account for even/odd alteration in reactivity, the new experimental feature was the emergence of CuAl_{22}^- as the most dominant “magic” peak. Taking aluminum as trivalent, the theoretical studies showed that the cluster containing 68 electrons has a filling sequence $1S^2|1P^6|1D^{10} 2S^2|1F^{14} 2P^4|2P^2 1G^{18} 3S^2 2D^8|2D^2$ where the D-shell is only partially filled. While partial filling of shells generally results in low HOMO-LUMO gap, the resistance to etching implied a large gap. Theoretical studies^{GP8} indicated that the ground state structure of CuAl_{22}^- can be described as an oblate structure with decreased height along the z axis relative to the width along the xy plane. The changes in the electronic structure can then be understood using the concept derived from crystal field splitting of atoms. Here the deformation of the cluster acts as a non-symmetric electric field that splits the spherical cluster shells. This is seen in Fig. 5 that shows the electronic structure of Al_{23}^- (Figure 5, Left panel) with 70 electrons and a closed shell sequence. The substitution of an Al by Cu results in an oblate structure with decreased height along the z axis. The result is a shell splitting due to ions in the lattice (Figure 5, Center panel) in which D_{xy} , and $D_x^2 - y^2$ would be degenerate and lowest in energy, D_{xz} and D_{yz} would be degenerate and of intermediate energy, and D_z^2 would be highest in energy (Fig. 5, central panel and Fig. 6). In

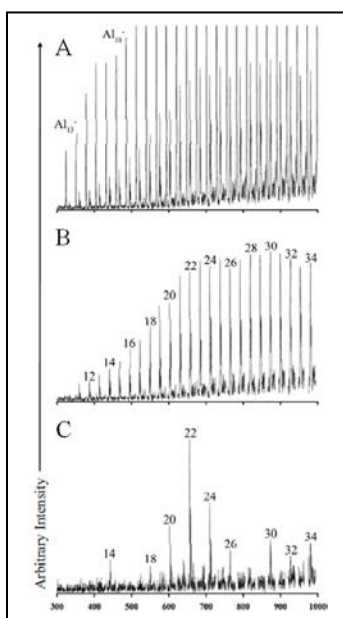


Fig. 4. : (A) Nascent distribution of Al_n^- and CuAl_n^- . (B) Nascent CuAl_n^- distribution (C) Oxygen-etched CuAl_n^- distribution.

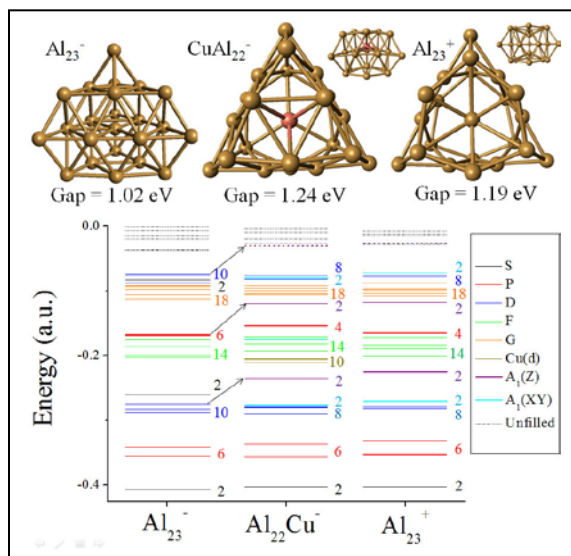


Fig. 5. Geometry and HOMO-LUMO Gaps of Left) Al_{23}^- , Center) CuAl_{22}^- and Right) Al_{23}^+ . Below, the electronic structure of A, B, and C with labeled shells. $A_1(XY)$ and $A_1(Z)$ indicate hybridized levels with extra nodes along the XY and Z planes.

fact, the unoccupied D_{z^2} state is almost 1.24 eV higher than HOMO and a large HOMO-LUMO gap results in an unusually non-reactive species for 68 electrons. Similar situation occurs for Al_{23}^+ that also has 68 electrons (see, Fig.5, right panel). We have recently extended demonstrated that the same mechanism can also account for the stability of CuMg_8^- and AuMg_8^- ^{Gp10} and plan to extend these findings to other clusters.

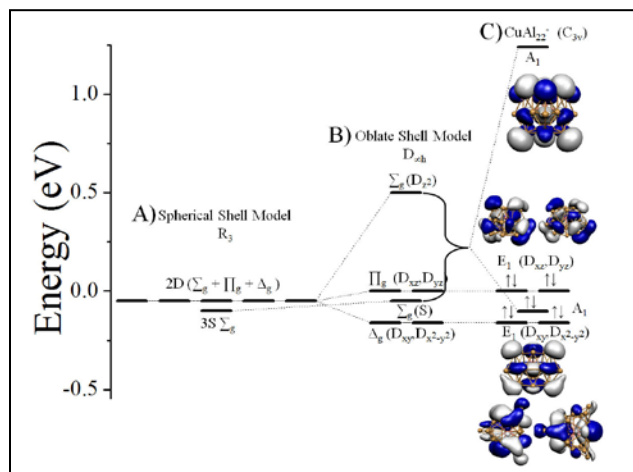


Figure 6. A) 2D and 3S spherical shell levels. B) Predicted crystal field splitting caused by negative point charges placed on opposite sides of the cluster along the Z axis, and C) the calculated splitting in CuAl_{22}^- using DFT.

B. Stable Aromatic Aluminum-Based Metal Clusters:

Aromaticity has historically been applied to organic systems that are cyclic, planar and contain $(4n+2)$ π electrons. Only recently has this concept been extended to all-metal systems, with the seminal work of Li et al. on the dianion Al_4^{2-} , studied experimentally and theoretically as MAl_4^- ($\text{M} = \text{Li}, \text{Na}, \text{or Cu}$). Our work on Al_3Bi yielded the first evidence of a neutral all-metal aromatic species, providing an attractive candidate for cluster assembly.^{GP6} This finding surfaced during our investigations of doped metal clusters where one or more heteroatom are incorporated into a metal framework. Taking aluminum as the metal, we investigated the stability of doped clusters where an Al atom was replaced by Bi, Sb, or As in a joint effort combining experimental negative ion photodetachment spectra and first principles theory.

Our studies on Al_nX ($n = 1-6$; $\text{X} = \text{Bi}, \text{As}, \text{Sb}$) led to two classes of stable clusters.^{GP6} The first category, consisting of Al_3X clusters, had planar configurations. The clusters had a low electron affinity, high ionization potential, larger HOMO-LUMO gaps, and required higher energy to remove an Al or X atom compared to their neighbors, all pointing to their stability. Theoretical investigations revealed that their stability was rooted in metallic aromaticity. Fig.7

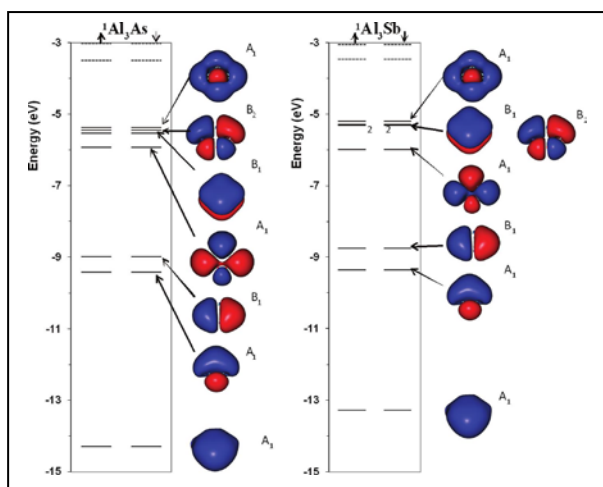


Fig. 7. One electron energy levels, isosurfaces (isovalue = 0.01 au), and symmetries of the molecular orbitals for the neutral Al_3As and Al_3Sb clusters.

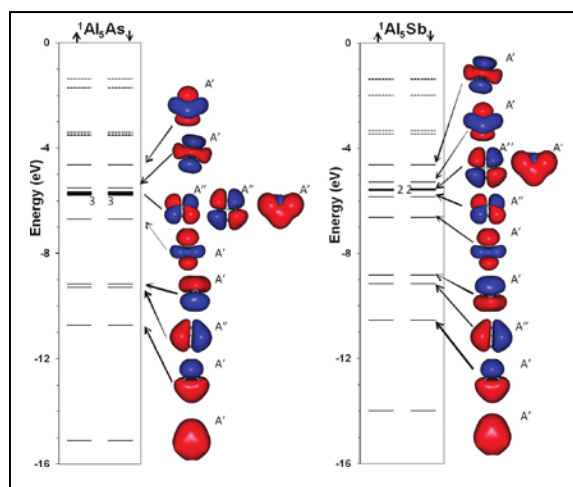


Fig. 8. One electron energy levels, isosurfaces (isovalue = 0.01 au), and symmetries of the molecular orbitals for the neutral Al_5As and Al_5Sb clusters.

shows the one electron levels, the isosurfaces, and the symmetries of the molecular orbitals for Al_3As and Al_3Sb clusters. In both cases, the HOMO-2 orbital is a delocalized π orbital with two electrons, satisfying the $(4n+2)$ π electron rule for aromaticity. Additionally, the HOMO and

HOMO-1 orbitals are σ delocalized orbitals resulting from the radially and tangentially oriented $p_{x,y}$ orbitals, respectively. These findings are reminiscent of the orbitals observed for the homoatomic species Al_4^{2-} and demonstrate how the p-orbitals in metallic clusters can combine to form stable species. The aromatic nature was further confirmed by studies of nucleus independent chemical shifts. The theoretical studies also indicated another class of stable species namely Al_5Bi , Al_5As and Al_5Sb . These clusters were found to have compact geometries. Each of these clusters contained 20 valence electrons, and their stability could be reconciled within a confined nearly free electron scheme with filled 1S^2 1P^6 , 1D^{10} , and 2S^2 shells (see Fig. 8).

The use of mixed clusters and the differing mechanisms of their stability offers a new freedom in designing new building blocks for cluster materials. In particular, through the choice of dopant substitute, one can design neutral or charged building blocks, a finding we wish to build on in the future work.

C. Reactivity of Aluminum Cluster Anions with Water: Mechanisms for H_2 Release.

A basic understanding of factors controlling the chemical reactivity of small atomic clusters is not only important for understanding fundamental science at reduced sizes, but also in exploiting unique properties of clusters in applications. As mentioned earlier, the variations in the reactivity of aluminum cluster anions with O_2 can be understood within a shell model where clusters like Al_{13}^- , Al_{23}^- , Al_{37}^- exhibit reduced reactivity because they have 40, 70, and 112 valence electrons which correspond to filled electronic shells with a large HOMO-LUMO gap. As our results show, not all oxidants are subject to the same fundamental constraints.

Recent effort on the reactivity of water with aluminum cluster anions, combining experiments in Castleman's group with theoretical investigations at VCU, brought out new mechanisms for reactivity in homoatomic species and highlighted the role of geometric factors on reactivity.^{GP3,GP7} In particular, it was found that (1) some clusters with open electronic shells such as Al_{20}^- do not reveal any significant reactivity with water while (2) selected clusters including even some with closed electronic sub-shells (Al_{23}^- , Al_{37}^-) exhibited strong reactivity towards water. Theoretical analysis shows that these behaviors are rooted in the non-uniform distribution of charge densities on cluster surfaces. Our initial findings, reported in a paper in *Science*,^{GP3} drew from the fact that the reactivity of aluminum clusters with nucleophiles, such as water depends strongly on the charge transfer tendencies of the surface sites and varies depending on the cluster's Lewis acidity at different sites on the cluster.^{GP7} As we show, the

reactivity entails a pair of complementary active sites (Fig. 9) one of which plays the role of Lewis base while the other acts as a Lewis acid^{GP7} and that their close proximity to each other

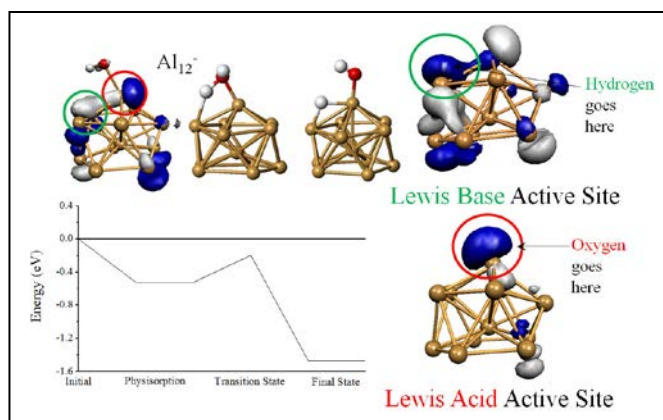


Figure 9. Lewis acid and Lewis base sites in an Al_{12}^- cluster. The O atom in H_2O binds to a Lewis

results in the splitting of the O-H bond and a higher reactivity. Figure 9 shows this splitting in Al_{12}^- , the smallest cluster to exhibit appreciable reactivity with H_2O . While similar behavior is known in metal oxides, this is the first time that this behavior has been observed in homoatomic clusters. We believe that our results illustrate a model case to identify active sites which have a propensity to accept or donate charge on the surface of the cluster and reveal how these sites may lead to novel reactive patterns.

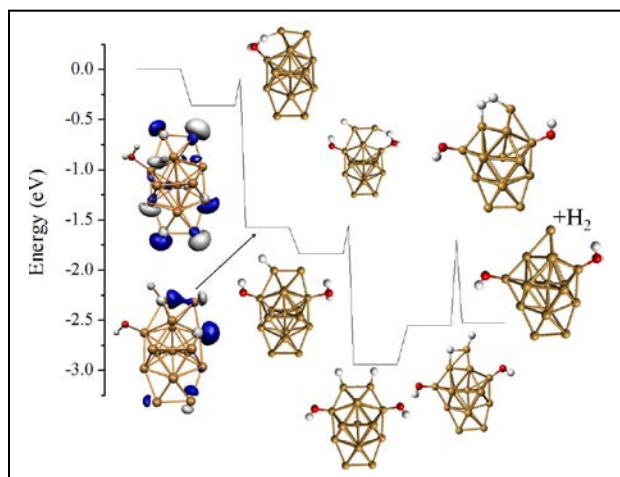


Fig. 10. Reaction coordinate for the formation of H_2 from Al_{17}^- and two H_2O molecules. The sequence is, a water chemisorbed to the cluster with HOMO charge density, the transition state to dissociative chemisorption, the resulting complex with LUMO+2 charge density. the second water chemisorbed to the adjacent Lewis-acid Lewis-base pair, the transition state, a complex with two dissociative chemisorbed waters. the complex rearranged to more efficiently release H_2 .

In addition to the proposal of breaking of OH bond as the primary mechanism for reactivity with H_2O , we also observed that specific clusters like Al_{16}^- , Al_{17}^- , and Al_{18}^- were absorbing two H_2O molecules and releasing H_2 . Our theoretical investigations revealed that such a reaction occurred through a cooperative process in clusters where the geometry resulted in a

pair of active sites on the two sides of the cluster.^{GP3} Figure 10 shows this for the case of Al_{17}^- that has Lewis acid active site on the left and on the right that absorb two H_2O molecules leading to two H atoms at the Lewis base sites on the top of the cluster. The two H-atoms combine to form the H_2 molecule that leaves the cluster.

These findings open pathways for using selected metal cluster ions to break polar covalent bonds to generate fine chemicals. We have recently demonstrated that such a mechanism can break other polar covalent bonds including carbonyl bond in formaldehyde.^{Gp11}

D. On the Growth Mechanisms of Nb_3C_n^- ($n=5-10$) Clusters:

Metallocarbohedrenes (Met-Cars) clusters consisting of 8 transition metal and 12 carbon atoms attracted considerable attention because of their unusual stability and caged structure. After their initial discovery in the group of Castleman, they have been proposed for various applications in nanotechnology including hydrogen storage and selective catalysis. In collaboration with Castleman's group, we investigated these potential building blocks of nanoassemblies and their growth mechanisms. The studies focused on photoelectron spectra of carbon-rich triniobium carbide clusters Nb_3C_n^- ($n = 5-10$) obtained at 308 nm in conjunction with calculations within the density functional framework to identify stable species synthesized in the laser vaporization source.

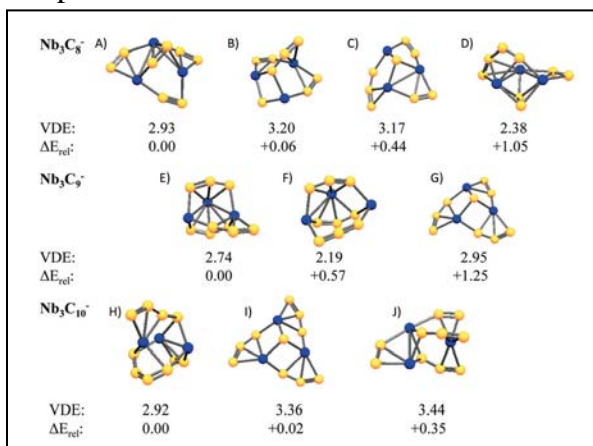


Fig. 11. The ground state and relevant isomer structures for Nb_3C_8^- , Nb_3C_9^- , and $\text{Nb}_3\text{C}_{10}^-$ clusters. The vertical detachment energies (VDE) and relative energies (ΔE) are also shown.

Our results showed the ability of triniobium carbide clusters to form multiple isomers, specifically structures that incorporate a lone “capping” carbon, molecular C_2 units, and previously unidentified C_3 and C_4 chains. The theoretical studies find three isomeric structural motifs. All Nb_3C_n^- clusters studied were three-dimensional structures (Fig. 11). One structural motif involves a central Nb_3 unit, in which the three niobium atoms are in a triangular configuration with a lone carbon atop the face of the Nb_3 triangular base, these structures are

referred to as “capping” motifs. This first motif was much like those found for the neutral smaller clusters reported previously for both niobium and tantalum carbide clusters. In the second major isomer-type, either a C_2 or C_3 unit resides in a bridging configuration across the Nb_3 triangular base, referred to as S-bridging. The final more dominant motif involves a dual (D-) bridging configuration, with a combination of C_2 , C_3 and/or C_4 bridging units across both the top and bottom faces of the base Nb_3 unit, referred to as D-bridging. Our studies accentuated the importance of the C_2 units, previously considered essential in the formation of Met-Cars. However, there are not only C_2 units present in the clusters, but a clear indication of longer C_n chains for the anionic clusters studied here. As the ratio of C to Nb atoms increase, the trend is to form larger C_n chains from C_2 to C_3 , thereby also encouraging metal-carbon bonding. More intriguing, we showed that clusters with an even number of carbon atoms, contain D-bridging structures with at least one C_4 -chain. This indicates a competition between C_2 , C_3 , and C_4 chains in $Nb_3C_n^-$ ($n = 5 - 10$). It remains to be seen if one can stabilize structures containing larger carbon chains into a bigger cage like framework.

E. From Free Clusters to Cluster Assembled Materials: Helical and Linear $[K(As_{11})]^{2-}$ Chains.

There has historically been a disconnect between magic clusters found in the gas phase and the synthetic assembly of clusters materials. Therefore, developing systematic guiding principles that can facilitate the transition from stable clusters to cluster solids is an important undertaking. While our final objective is to create assemblies based on aluminum or other high energy materials, we collaborated with Sen and co-workers to formulate protocols that may enable synthesis of the cluster assemblies and to explore the potential offered by such cluster

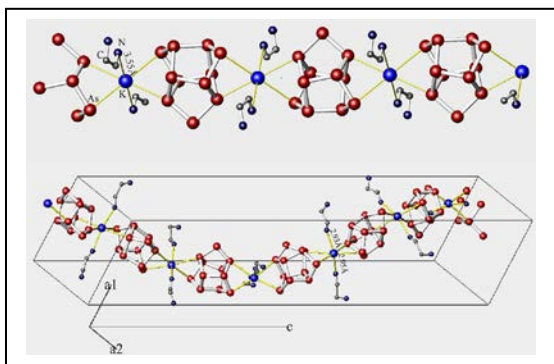


Fig. 12. The linear and helical chains in $As_{11}K_3$ Cluster assembled solid. The ethylenediamine (solvent) are also shown.

solids. To this end, Sen et al. succeeded in synthesizing two different architectures^{GP4} using the same building blocks, namely As_{11} and K, by using different concentrations of the solvent. Two

chains of $[\text{K}(\text{As}_{11})]^{2-}$ clusters, one helical and one linear, were synthesized and characterized by X-ray crystallography. The pitch of the helix is 52.05 Å and includes six $[\text{As}_{11}]^{3-}$ clusters. The stoichiometries of the two conformations differ only in the number of solvent molecules: 3 ethylenediamine molecules per As-cluster for the helix and 2 for the straight chain. In both cases, two solvent molecules are interacting with the potassium cations which link the Arsenic clusters. Theoretical investigations in our group revealed that the origin of the two local arrangements is due to solvent interactions. Without solvent, the calculations show that the linear chain is more stable, as the K-As₁₁ distances are minimized. With solvent, the helix's increase spacing between the K cation and As₁₁, which enhances binding between ethylenediamine and the potassium cations in the chain, stabilizes the helical assembly. Electronic structure calculations indicated that both the linear and helical structures have band gaps of 1.71 eV and 1.68 eV respectively, in agreement with measured values. However, the helicity does affect the electronic transport properties. We plan to extend this base of knowledge to stabilize aluminum based assemblies.

III. Theoretical Methods

All theoretical studies described in the report are first principles and carried out within the ab initio self-consistent field linear combination of atomic orbitals-molecular orbital (SCF-LCAO-MO) method. The molecular orbital (MO) is expressed as a linear combination of atomic orbitals (LCAO) centered at individual atomic sites or in a numerical form over a mesh. The combination coefficients are determined by solving the Hohenberg-Kohn-Sham density functional equation self-consistently. The exchange-correlation contribution to the potential will be treated using the latest gradient-corrected functionals. We have used NRLMOL developed at NRL by Pederson and co-workers with whom we have long standing collaboration, and deMon, originally developed by Salahub with continued development by Koster – a recent collaborator. These codes allow both all-electron and pseudopotential calculations and are massively parallel. NRLMOL allows treatment of spin-orbit coupling, and can treat clusters containing 100-200 atoms, while deMon can optimize and provide electronic structure for clusters of 500 atoms. For clusters and adsorbates on surfaces, periodic DFT is needed, and for this we have used the Vienna ab-initio simulation package (VASP), currently used in the our group to study cluster assembled materials. For all calculations, ground state geometries will be optimized by starting from multiple starting geometries and relaxing to the minimum energy configuration. We have used these codes over the past several years and have considerable knowledge about their limitations and accuracy.

IV. Khanna group publications (GP) from 2009-2011, supported by AFOSR.

- GP1.** “Clusters, Superatoms and Building Blocks of New Materials”, A. W. Castleman, Jr. and S. N. Khanna, Invited Featured Article for the *Journal of Physical Chemistry C*, **113**, 2664-2675 (2009).
- GP2.** “Photoelectron imaging and theoretical investigation of bimetallic $\text{Bi}_{1-2}\text{Ga}_{0-2}^-$ and Pb_{1-4}^- cluster anions”, M. Sohby, J. U. Reveles, U. Gupta, S. N. Khanna, and A. W. Castleman, Jr., *J. Chem. Phys.* **130**, 492 (2009).
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